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Effective quenching and excited-state relaxation of a Cu(I) photosensitizer addressed by time-resolved spectroscopy and TDDFT calculations

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A B S T R A C T

Homogenous photocatalytic systems based on copper photosensitizers are promising candidates for noble metal free approaches in solar hydrogen generation. To improve their performance, a detailed understanding of the individual steps is needed. Here, we study the interaction of a heteroleptic copper (I) photosensitizer with an iron catalyst by time-resolved spectroscopy and ab initio calculations. The catalyst leads to rather efficient quenching of the ³MLCT state of the copper complex, with a bimolecular rate being about three times smaller than the collision rate. Using control experiments with methyl viologen, an appearing absorption band is assigned to the oxidized copper complex demonstrating that an electron transfer from the sensitizer to the iron catalyst occurs and the system reacts along an oxidative pathway. However, only about 30% of the quenching events result in an electron transfer while the other 70% experience deactivation indicating that the photocatalytic performance might suffer from geminate recombination.

1. Introduction

The rapid technical progress and the increasing energy demand of modern human society leads to an accelerated depletion of exhaustible resources [1]. To cope with this situation, alternative energy sources must be explored. In the recent decades, substantial progress on wind and solar energy has been achieved. However, this energy has limited possibilities to be stored and reused on demand. A reasonable solution would be to switch to hydrogen as an energy storage reservoir [2–4]. In 1972, the principal capability to obtain hydrogen directly by light-driven decomposition of water was demonstrated [5]. Nowadays, there exist various photocatalytic water-splitting systems based on precious metals (for reviews, see [6–9]), for other studies suggesting the use of simple redox-active chromophores such as quinones, see ref. [10]). In contrast, noble-metal free systems are not as widely explored, for selected examples, see [11–13].

To make further progress in developing novel photocatalytic systems with good performance, high efficiency, and long-term stability, detailed investigations of the underlying elementary physical and chemical processes are necessary since the rational design of the systems calls for a microscopic understanding [14]. Knowledge on peculiarities of the single steps in the entangled photo-activated catalytic cycle such as absorption of light, electron transfer, and oxidation/reduction

reactions will facilitate targeted changes and optimizations of the existing systems. In multi-component systems, the efficiency depends primarily on the electron transfer between various components. Very often, the quenching rates reported for catalytic systems are quite high, but it should be taken into account that electron transfer is only one possible channel of quenching. Exemplarily, for catalytic systems, energy transfer and collisional deactivation might also be possible. For instance, in ref. [15], we found for the case of an Ir(III) photosensitizer that electron transfer is inhibited by the energetic mismatch between the relevant electronic states. Despite this fact, collisions with an iron catalyst result in efficient quenching. For this reason, it is of high importance to differentiate between electron transfer and other processes.

In this paper, we study a homogeneous noble-metal free model system comprising of iron carbonyl [HFe₃(CO)₁₁][HNEt₃] (Et = CH₂CH₃) (Fe-cat) as water-reduction catalyst [16] and a heteroleptic copper(I) photosensitizer (CuPS) [17,18] comprised of a xantphos and a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand [13,19] (for the structure, see Fig. 1). This system was chosen since it represents one of the very few optimized homogenous water-reduction systems completely based on non-precious metals. One has to admit that the overlap of the absorption spectrum of the CuPS with the solar spectrum is very poor. Nevertheless, the system still shows some activity if an UV cut-off filter is inserted in the illumination path, although at a much

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